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<b>(21) International Application Number:</b> PCT/US98/00501 <b>(22) International Filing Date:</b> 9 January 1998 (09.01.98) <b>(30) Priority Data:</b> 08/778,147 10 January 1997 (10.01.97) US <b>(71) Applicant:</b> DONLAR CORPORATION [US/US]; 6502 South Archer Avenue, Bedford Park, IL 60501-9998 (US). <b>(72) Inventors:</b> KOSKAN, Larry, P.; 8617 Golfview Drive, Orland Park, IL 60462 (US). MEAH, Abdul, Rehman, Y.; Apartment 21-203, 8350 S. 86th Avenue, Justice, IL 60458 (US). SANDERS, J. Larry; 13044 W. Choctaw Trail, Lockport, IL 60441 (US). ROSS, Robert, J.; 658 Hawthorne Avenue, Elmhurst, IL 60126 (US). <b>(74) Agents:</b> CEPURITIS, Talivaldis et al.; Olson & Hierl, Ltd., 36th floor, 20 North Wacker Drive, Chicago, IL 60606 (US).		<b>(81) Designated States:</b> AT, AU, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, GB, HU, IL, JP, KE, KR, KZ, MG, MX, NO, NZ, PL, PT, RU, SE, SK, TR, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD AND COMPOSITION FOR ENHANCED PLANT PRODUCTIVITY  <b>(57) Abstract</b>  This invention relates to enhancing plant productivity employing a method and improved compositions containing water-soluble cross-linked polyamino acids having a weight average molecular weight of a size larger than about 1,500. More particularly, cross-linked polyamino acids enhance plant productivity when supplied to the plant directly as the free acid or salt thereof or hydrolyzed from a cross-linked precursor of the cross-linked polyamino acid by the method disclosed. Particularly suitable for this purpose are water-soluble, cross-linked polyaspartic acid, and salts thereof and hydrolyzed cross-linked polysuccinimide.		

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**METHOD AND COMPOSITION FOR  
ENHANCED PLANT PRODUCTIVITY**

Cross-Reference to Related Application

5           This application is a continuation-in-part of  
co-pending U.S. Serial No. 08/313,436, filed on  
September 27, 1994, now U.S. Patent No. 5,593,947, which  
is a continuation-in-part of U.S. Serial No. 07/972,375,  
filed on November 5, 1992, now U.S. Patent No.  
10   5,350,735.

Technical Field

          This invention relates to a method and  
composition for enhancing the productivity of plants.  
More particularly, this invention relates to absorption  
15   phenomena that facilitate the assimilation and  
utilization of nutrients by plants through either seed,  
root or foliar pathways.

Background of the Invention

          Organic acids and oligomers thereof have been  
20   shown to promote plant growth. Typical promoters of  
plant growth are described by Kinnersley et al., Plant  
Growth Regulation, 9, pp. 137-146 (1990) (lactic acid  
and relatively low molecular weight oligomers of lactic  
acid); in U.S. Patent No. 4,813,997 to Kinnersley et al.  
25   (oligomers of glycolic and/or L-lactic acid) and in U.S.  
Patent No. 4,799,957 to Danzig et al. (oligomers of  
thiolactic and thioglycolic acids). All of the forgoing  
approaches to plant growth promotion appear to focus on  
coordination as a means for increasing plant uptake of  
30   compounds vital to the growth of the plant, e.g.,  
micronutrients such as calcium, magnesium, sulfur,  
manganese, zinc, copper, iron, boron, and the like.

          A common approach to promoting plant growth  
has been, and continues to be, the use of nutrients  
35   (fertilizers), natural as well as synthetic. Synthetic

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nutrients usually provide nitrogen in a plant-usable form, such as urea for example, and/or inorganic nitrates, phosphates, or the like compounds. While such nutrients may be applied, more or less, at the convenience of the farmer, and may be applied as often as deemed desirable, the overuse of synthetic nutrients and the inefficient use of synthetic nutrients are major factors responsible for environmental problems such as eutrophication of groundwater, nitrate pollution, phosphate pollution, and the like. An overview of the undesirable effects of nitrogen fertilizer is presented by Byrnes, Fertilizer Research, 26, pp. 209-215 (1990).

To ameliorate the problems attendant to inefficient nutrient use and nutrient overuse, there is an ongoing desire and need for environmental and production reasons to increase fertilizer efficiency and enhance plant productivity. There is a need, therefore, to maximize the availability, uptake and utilization of plant nutrients while minimizing loss of nutrients or fertilizer elements through leaching, denitrification, vaporization and other mechanisms that prevent assimilation of these nutrients by the biological and physical mechanisms of plants.

The present invention addresses and resolves these problems by methods and compositions which provide a favorable environment for enhancing the utilization of nutrients by germinating or growing plants resulting in enhanced plant productivity.

#### Summary of the Invention

The present invention provides a method and improved compositions for enhanced plant productivity by achieving more efficient utilization of nutrients.

The present method comprises supplying to a plant a composition containing a productivity enhancing amount of a water-soluble, crosslinked polyamino acid

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having a weight average molecular weight (Mw) such that it is not absorbed by the plant, i.e., larger than about 1,500. The crosslinked polyamino acid can be supplied in the form of the free acid or salt thereof or can be  
5 hydrolyzed from a precursor thereof which is water soluble and has a weight average molecular weight (Mw) larger than about 1,500. The method as practiced provides a more favorable environment for assimilation and utilization of nutrients by the plant, via its seed,  
10 root feeding zone, foliar mechanisms for absorption and translocation, growth medium or combinations thereof.

The crosslinked polyamino acid can be supplied to the plant directly or as a crosslinked precursor of polyamino acid which can hydrolyze in situ in an  
15 alkaline moist or wet environment to a crosslinked polyamino acid. Particularly preferred is water-soluble crosslinked polyaspartic acid and salts thereof and its precursor, crosslinked polysuccinimide. The crosslinked polyamino acid or salt thereof can be supplied  
20 separately or in combination with fertilizer.

Preferred crosslinked polyaspartic acid is prepared from polyaspartic acid having aspartic acid residues of at least 20% of the total number of residues in the polymer. Crosslinked polyaspartic acids  
25 preferably have, prior to crosslinking, at least 15 repeating amino acid units or mers in the polymer chain.

The crosslinked polyamino acids also can be used in combination with uncrosslinked polyamino acids and water-soluble, non-peptidal polymers.

30 The method and compositions of this invention beneficially provide stress protection to plants and promote growth in environments containing salts present in concentrations that are normally toxic to plants. Further, a more favorable environment is provided which  
35 supplies the nutritional elemental requirements to the

plant employing nutritional levels that are lower than are required with conventional fertilizers.

#### Brief Description of the Drawings

5 In the drawings, there are shown photographic reproductions of corn plants treated in a particular manner alongside a control corn plant. In each case a yardstick (36 inches) is shown positioned between the photographed plants to indicate scale. In particular,

10 FIGURE 1 shows corn plants 40 days after planting, and treated with one-third of the recommended fertilizer dosage alongside a corn plant treated with the recommended dosage for the same fertilizer;

15 FIGURE 2 shows a corn plant 40 days after planting, one treated with one third of the recommended fertilizer dosage alongside a corn plant similarly treated with the same fertilizer but also with 10 parts per million by weight of polyaspartic acid;

20 FIGURE 3 shows corn plants 40 days after planting, both treated with the recommended fertilizer dosage and one plant also with 10 parts per million by weight of polyaspartic acid;

25 FIGURE 4 shows corn plants 40 days after planting, one treated with the recommended fertilizer dosage and the other with one-third of the recommended fertilizer dosage but also with 10 parts per million by weight of polyaspartic acid; and

FIGURE 5 is a graphical representation of growth enhancement with polyaspartic acid.

#### Detailed Description of Preferred Embodiments

30 The present invention is directed to a method and improved compositions for enhancing plant productivity. Enhanced plant productivity is achieved by making nutrients more readily available to the plant through its seed, root feeding zone, foliar absorption  
35 and translocation mechanisms, its growth medium or

combinations thereof. Thus a more favorable environment is provided for increased assimilation and efficient utilization of applied natural or chemical nutrients by plants.

5           The present invention in its various aspects, is predicated, in part, on the discovery that polymeric acids, and polymeric amino acids in particular, of a molecular size too large to enter a plant nevertheless can provide a favorable environment for enhanced plant  
10           productivity. The more efficient utilization of nutrients can be realized in the presence of the polymeric acid inasmuch as relatively lower nutrient dosages can be relied upon to provide the requisite nutrients to the plant.

15           The term "enhanced plant productivity" as used herein means that at least one or more of the following factors is achieved: increased growth rate, increased biomass, higher yields and quality (i.e., increased  
20           protein content), accelerated rate of root formation, increased tillering, increased chlorophyll concentration and the like indicia.

          The term "crosslinked polyamino acid" as used herein includes water-soluble salts of the crosslinked polyamino acid. Preferred crosslinked polymeric amino  
25           acids of the present invention may contain aspartic acid monomer units linked by alpha peptide bonds, beta peptide bonds or both and/or glutamic acid monomer units linked by alpha peptide bonds, gamma peptide bonds or both.

30           The term "crosslinked polysuccinimide" as used herein refers to substantially water-soluble random copolymers comprised of succinimide units and structural units derived from a monomeric crosslinking agent. Crosslinked polysuccinimide preferably contains  
35           substantially no alpha-aspartate and beta-aspartate

units or a relatively small proportion thereof such that the combined amount of alpha-aspartate and beta-aspartate units is less than about 20% of the polymer. The amount of crosslinking is limited to the extent that crosslinking does not materially affect the solubility of the crosslinked polyaspartic acid produced when crosslinked polysuccinimide is subsequently hydrolyzed in an alkaline aqueous medium.

More particularly, the present invention is directed to employing a productivity enhancing amount of crosslinked polyamino acid or hydrolyzable crosslinked precursor thereof. The degree to which the polyamino acid is crosslinked is limited only to the extent that crosslinking does not materially affect the solubility of the crosslinked polymer moiety in polar solvents, such as water, alcohol or mixture thereof.

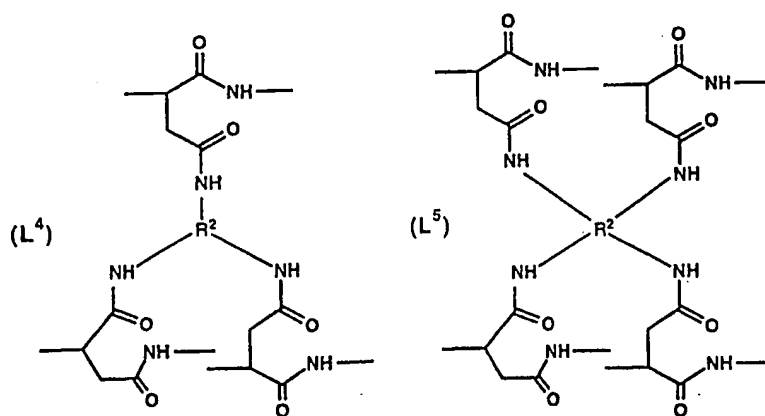
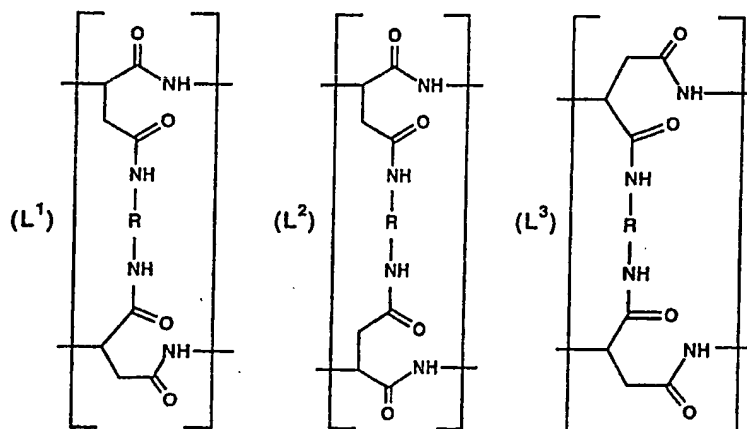
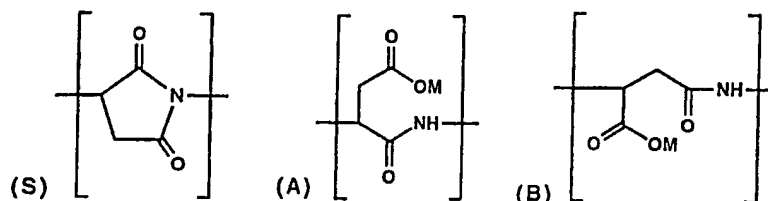
A preferred polyamino acid in crosslinked or uncrosslinked form which is well suited for the practice of this invention to provide more efficient utilization of both natural and synthetic plant nutrients is polyaspartic acid. This polymer can be conveniently prepared from L-aspartic acid, D-aspartic acid or DL-aspartic acid, or from aspartic acid precursors (ammonium maleate, maleamic acid, ammonium malate, diammonium maleate, diammonium malate, ammonium maleamate, ammonium fumarate, diammonium fumarate) using thermal condensation methods.

Crosslinked polyamino acids are preferably water soluble and produced from polyaspartic acid moieties containing aspartic acid monomer units linked by  $\alpha$  peptide and  $\beta$  peptide bonds and structural units derived from a monomeric crosslinking agent.

Useful crosslinked polyaspartic acids are random copolymers structurally comprised of monomer units of succinimide (structural formula S),



alpha-aspartate (structural formula A), beta-aspartate (structural formula B) and crosslinking dimeric aspartamides (structural formula having any one of the following three structural formulas, L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>),  
 5 trimeric aspartamides (having the structural formula L<sup>4</sup>) or tetrameric aspartamides (having the structural formula L<sup>5</sup>). For convenience, these will be referred to collectively as structural formula (L).



In the structural units, (A) and (B), M can be a hydrogen ion, an alkali metal cation such as Na<sup>+</sup>, K<sup>+</sup> or Li<sup>+</sup>, an ammonium ion, or quaternary ammonium ion. The term "crosslinked polyaspartic acid" and its various grammatical variations as used herein includes water-soluble salts of crosslinked polyaspartic acid.

In the structural (L) units, (L<sup>1</sup>), (L<sup>2</sup>) and (L<sup>3</sup>), R is a divalent organic linking group derived from an organic crosslinking agent, preferably containing 1 to about 20 carbon atoms and optionally aliphatic and/or aromatic ring structures. The organic crosslinking agent preferably is an organic base containing at least two primary amine groups capable of reacting with a succinimide monomer unit to form a crosslink thereof, for example, aliphatic diamines, such as ethylene diamine (EDA), 1,3-bis(aminoethyl)cyclohexane (1,3-BAC), and hexamethylene diamine (HMDA); arylaliphatic diamines, such as meta-xylylenediamine (MXDA); and polyether diamines, such as polyoxyalkylene diamines and amine terminated block copolymers of polyoxyalkylene/polyalkylene glycols, amine terminated polypropylene glycols having an average of from about 2 to about 68 propylene oxide units, amine terminated polyethylene/polypropylene glycols, triethylene glycol diamine and tetraethylene glycol diamine, amine terminated polyalkyleneimines, such as diethylene triamine (DETA) and tetraethylene pentamine (TEPA).

In the respective structural formula (L) units, (L<sup>4</sup>) and (L<sup>5</sup>), R<sup>2</sup> is a trivalent and tetravalent organic linking group derived from triamino, tetraamino and polyamino crosslinking agents, such as tris(2-aminoethyl)amine (TAEA), polyamines and propylene oxide based triamines varying in molecular weight from about 440 to about 5,000 and polyvinylamine polymers.

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For convenience, reference to the term "(L) units" includes any one of the monomeric crosslinking (L) structural units without limitation.

The terms "crosslinked polyaspartate" or  
5 "crosslinked polyaspartic acid" are used interchangeably herein to refer to such water-soluble random copolymers structurally comprised primarily of (A), (B) and (L) units having a weight average molecular weight (Mw) larger than about 1,500, more preferably of at least  
10 about 2,000. Crosslinked polyaspartates preferably contain no (S) units or relatively small proportions of less than about 20%.

Counterions for polyaspartates include, but are not limited to, the alkali metal ions, preferably  
15 Na<sup>+</sup>, K<sup>+</sup>, and Li<sup>+</sup>; alkali earth metal cations, preferably Mg<sup>++</sup>, Ca<sup>++</sup> and Ba<sup>++</sup>; transitional metal ions, preferably Zn<sup>++</sup>, Co<sup>++</sup>, Fe<sup>++</sup> and Fe<sup>+++</sup> and NH<sub>4</sub><sup>+</sup>.

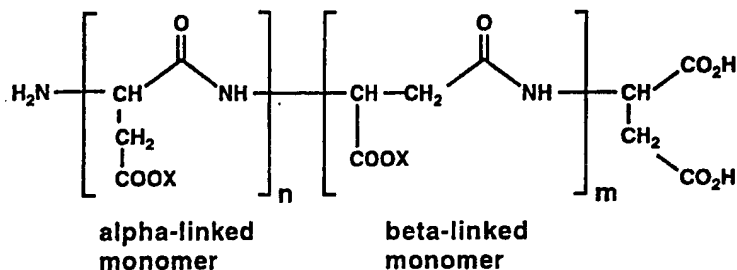
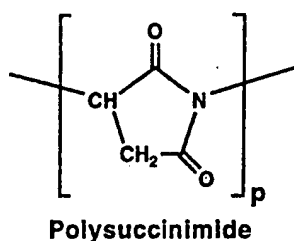
Water-soluble crosslinked polyaspartic acid and crosslinked polysuccinimide useful as hydrolyzable  
20 precursors can be synthesized by any method. For example, preferred soluble crosslinked polyaspartates and crosslinked polysuccinimides of varying Mw can be produced by the method described in U.S. Patent No. 5,552,516 to Ross et al., incorporated herein by  
25 reference, or can be produced by well known free radical crosslinking techniques. Presently preferred, but not limited thereto, are the sodium salt of polyaspartic acid crosslinked with 10 mol% meta-xylylenediamine, preferably having a Mw of about 80,000 and the sodium  
30 salt of a copolymer of 80 mol% aspartic acid/20 mol% N-allylaspartamide free radical crosslinked with hypophosphite, preferably having a Mw of about 53,311.

The crosslinked polyamino acids can also be used in combination with water-soluble uncrosslinked  
35 polyamino acids, such as polyaspartic acid, polyglutamic

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acid, polysuccinimide, polylactic acid, polyglycolic acid and mixtures thereof.

Polysuccinimide and polyaspartic acids useful, directly or in crosslinked form, in this invention are represented by the following structures:



where X = H<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>+</sup>, Zn<sup>++</sup>, Co<sup>++</sup>, Li<sup>+</sup>, Ba<sup>++</sup>, Fe<sup>++</sup>, Fe<sup>+++</sup> and the value of the integers n, m and p are such that the copolymer and polymer, if present, has a weight average molecular weight larger than about 1,500 daltons.

The polyaspartic acid moieties contain aspartic acid monomer units linked by α peptide and β peptide bonds. A preferred polyaspartic acid is β-polyaspartic acid, i.e., one having > 50 mole % of aspartic acid units linked by β peptide bonds and < 50 mole % of aspartic acid units linked by α peptide bonds. Preferably, 60-80 mole % of the polyaspartic acid is in β-linkage form and the polyaspartic acid has a Mw within the range of 2,000-100,000. More preferably, approximately 70 mole % to 80 mole % of the polyaspartic

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acid has  $\beta$  form and has a Mw within the range of 2000-20,000. Most preferably, approximately 70 mole % to 75 mole % of the polyaspartic acid has  $\beta$  form and 25 mole % to 30 mole %  $\alpha$ , and has a Mw within the range of 2000-5000.

A preferred polyaspartic acid moiety is  $\beta$ -polyaspartic acid, i.e., one having >50 mole % of aspartic acid units linked by  $\beta$  peptide bonds and <50 mole % of aspartic acid units linked by  $\alpha$  peptide bonds. Preferably, 60-80 mole % of the polyaspartic acid moiety is in  $\beta$ -linkage form and the polyaspartic acid moiety has a Mw within the range of about 2,000 to about 100,000. More preferably, approximately 70 mole % to 80 mole % of the polyaspartic acid moiety has  $\beta$  form and has a Mw within the range of about 2,000 and about 20,000. Most preferably, approximately 70 mole % to 75 mole % of the polyaspartic acid moiety has  $\beta$  form and 25 mole % to 30 mole %  $\alpha$  form, and has a Mw within the range of 2,000-5,000.

In general, the water soluble but crosslinked polymeric amino acids can be made available to the plant in the form of aqueous liquids or in substantially solid form and supplied to the plant by any convenient manner of application.

Preferably, aqueous nutrient solutions supplied to the plant contain at least about 10 parts per billion (ppb) by weight, preferably about 0.1 to about 1,000 parts per million (ppm) by weight, more preferably about 1 to about 500 ppm by weight, of the crosslinked polymeric amino acid with or without uncrosslinked polymeric amino acid present in the solution. Such solutions can be applied to the soil surrounding the plant so as to contact the plant's root system, can be applied to the plant's foliage utilizing usual foliar feeding techniques, can be introduced into

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hydroponic gardening or farming systems, and in any other convenient manner. For example, such solutions can be sprayed or otherwise applied to contact the roots, stems, or leaves of the plants whose productivity, growth and/or development is to be enhanced, as well as to the seeds or reproductive parts of these plants, in an amount as is discussed in greater detail hereinbelow.

Aqueous nutrient solutions containing the crosslinked polymeric amino acid, preferably derived from polyaspartic acid, are also useful to enhance effective plant productivity under stressful growth limiting conditions, e.g., in soil that contains salts or metal ions in concentrations normally toxic to plants, soil depleted in certain nutrients, etc.

The crosslinked polymeric amino acids, with or without uncrosslinked polyamino acid, preferably derived from polyaspartic acid, can also be applied to soil in substantially solid form alone or in combination with nutrients. For example, granular, pelletized, dust or powdered forms of the crosslinked polyamino acids can be applied by gravity or air blast equipment into the furrow, row or site at seeding or planting time. Dry granular or pelleted forms of the crosslinked polyamino acids, preferably derived from polyaspartic acid, can be impregnated or pre-formed as carriers of nutrients and can then be used for surface application by ground rig or aircraft.

The crosslinked polymeric amino acids, like uncrosslinked polymeric amino acids, can be supplied to the plant as a precursor in an anhydrous form, as for example crosslinked polysuccinimide (preferably derived from anhydropolyaspartic acid). In combination with a basic material in the presence of water, soil moisture, rainfall, etc. such precursors can hydrolyze in situ to

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crosslinked polyaspartic acid and salts thereof. Basic materials which can be used are sodium carbonate, sodium bicarbonate, limestone, ammonia and the like.

5 Crosslinked polysuccinimide can be applied and mixed with the solid basic material in powder, pellet or granule form or can be incorporated into an aqueous growth medium, such as a hydroponic medium, preferably under alkaline conditions.

10 For example, crosslinked polysuccinimide can be mixed with sodium carbonate or sodium bicarbonate and applied as a powder, as a dry granule or in pellet form. The sodium carbonate and sodium bicarbonate will hydrolyze crosslinked polysuccinimide to crosslinked polyaspartic acid sodium salt in moist or wet soil.

15 Crosslinked polysuccinimide can also be applied to soil as a powder, pellet or as granules mixed with limestone (Ca and Mg carbonate). In this application, the carbonates of the limestone can hydrolyze the crosslinked polysuccinimide to crosslinked polyaspartic acid sodium salt in moist or wet soil.

20 Another way of using crosslinked polysuccinimide is to apply it to soil as a powder, granule or pellet after the soil has received an injection of ammonia. In this process, ammonium hydroxide formed from the ammonia and water in the soil will hydrolyze the crosslinked polysuccinimide to crosslinked polyaspartic acid.

25

The polymeric amino acids from which crosslinked polymeric amino acids can be produced, to be suitable for the practice of the present invention, must be or become water soluble, and have a molecular size

30 sufficiently large to preclude absorption into the plant's own system. To that end, the polymeric amino acids and crosslinked polymeric amino acids deemed suitable for the present purposes, while hydrophilic, have a Mw larger than about 1,500 and have at least

35

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about 15 repeating amino acid units (residues), or mers, in the linear polymer chain that constitutes the polymeric amino acid prior to crosslinking. Suitable linear polymer chains are crosslinked to a degree that does not materially affect the water solubility of the resulting crosslinked polymeric moiety.

Polymeric amino acids having a molecular size in excess of about 100,000 Mw usually do not exhibit adequate solubility in water for the present purposes. Thus a polymeric amino acid or crosslinked polymeric amino acid of a molecular size not larger than about 100,000 Mw is presently preferred. A useful molecular size is in the range of about 1,500 to about 85,000 Mw, preferably in the range of about 1,600 to about 85,000 Mw, more preferably in the range of about 1,700 to about 60,000, most preferably in the range of about 2,000 to about 30,000 Mw.

Illustrative useful polymeric amino acids from which crosslinked polymeric amino acid can be produced include, but are not limited to, those having side chains containing carboxylic acid, thiocarboxylic acid, mercapto, hydroxy, imidocarboxy, and/or amino moieties. Preferred such polymeric amino acids or salts thereof can be selected from the group consisting of polyaspartic acid, polyglutamic acid, polylysine, polyglycine, polycysteine, polyserine, copolymers thereof, such as polycysteine/glutamic acid and terpolymers thereof, such as polycysteine/glutamic/aspartic acid. Also useful are block or random copolymers or terpolymers of polyamino acids and non-amino organic acids, such as a block copolymer of aspartic acid residues and L-lactic acid residues, a random copolymer of aspartic acid residues and glycolic acid residues, a conjugated protein constituted by amino acid residue chains interconnected



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by one or more polycarboxylic acid residues, mixtures of the foregoing, and the like.

Also useful is polysuccinimide supplied directly or in water-soluble crosslinked form or a  
5 copolymer containing succinimide residues and partially hydrolyzed polysuccinimide which can be hydrolyzed in situ to polyaspartic acid, crosslinked polyaspartic acid or mixtures thereof.

The polymeric amino acids and crosslinked  
10 polymeric amino acids of this invention can be used in combination with water-soluble, non-peptidal polymers to provide more efficient utilization of both natural and synthetic plant growth nutrients.

Examples of water-soluble, non-peptidal  
15 polymers which can be used include, but are not limited to, water-soluble, non-peptical polycarboxylates, such as polylactic acid, polyglycolic acid, polyacrylic acid, polymaleic acid, polyitaconic acid, and polymethacrylic acid, polyacrylamide and copolymers thereof such as, but  
20 not limited to, acrylamide-acrylic acid copolymers, acrylamide/2-acrylamido-2-methylpropanesulfonic acid copolymers, acrylamide/diallyldimethylammonium chloride copolymers, acrylamide/dimethylaminoethyl methacrylate and acrylate copolymers and methyl chloride or sulfate  
25 quaternized derivatives of these copolymers, acrylic acid/maleic acid copolymers, acrylic acid/itaconic acid copolymers, maleic acid/itaconic acid copolymers, methacrylic acid/acrylamide copolymers, methacrylic acid/acrylic acid copolymers polyvinyl alcohols and  
30 polyvinylpyrrolidone.

The water-soluble, non-peptidal polymers which can be used in combination with the polyamino acids and crosslinked polyamino acids should have a molecular size larger than about 1,500 Mw and preferably have at least  
35 about 15 repeating monomer units, or mers, in the linear

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polymer chain that constitutes the water-soluble polymer. For present purposes, a water-soluble polymer of molecular size not larger than about 100,000 Mw is preferred.

5 Polymeric amino acids suitable for use in the present invention can be made, inter alia, by thermal condensation methods. See, for example, U.S. Patent No. 5,057,597 to Koskan; U.S. Patent No. 5,221,733 to Koskan et al.; U.S. Patent No. 5,219,952 to Koskan et al.;  
10 Little et al., American Chemical Society, 97, 263-279 (1991) and U.S. Patent No. 4,696,981 to Harada et al.

The starting materials for the polymerization, i.e., the amino acid monomers, can exist as optical isomers and can be polymerized either as a racemic  
15 mixture or as segregated optical isomers.

Particularly well suited for the practice of the present invention, and from which crosslinked polyamino acids can be prepared, are the polyamino acids such as polyaspartic acid having a Mw in the range of  
20 about 3,000 to about 100,000, polyglutamic acid having a Mw in the range of about 4,000 to about 14,000, polyglycine having a Mw in the range of about 1,500 to about 7,000, and polylysine having a Mw in the range of about 2,000 to about 7,000.

25 The aforesaid polyamino acids and crosslinked polyamino acids thereof increase the efficiency of utilization of nutrients, both natural and synthetic. The nutrients can be those found naturally in the soil or plant growth medium or can be those which are added  
30 or can be those that are residual nutrients from previous nutrient treatments. More efficient utilization by the growing plants of both macronutrients, such as but not limited to, nitrogen (N), phosphorus (P), potassium (K) and micronutrients,  
35 such as but not limited to, calcium (Ca), magnesium

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(Mg), sulfur (S), zinc (Zn), iron (Fe), manganese (Mn), boron (B), cobalt (Co), molybdenum (Mo), copper (Cu) and nickel (Ni) is accomplished by employing the polyamino acids and crosslinked polyamino acids of this invention.

5           There are many uses and applications for the present inventions in its various aspects. Illustrative are uses in agriculture, gardening, horticulture, hydroponics, forestry, land reclamation (e.g., landfills, soils with relatively high salt  
10 concentrations, etc.), and the like.

          Suitable dosage rates of crosslinked or uncrosslinked polymeric amino acid component of the present invention, so as to provide a sufficient productivity enhancing amount of crosslinked or  
15 uncrosslinked polymeric amino acid to the plant to enhance nutrient utilization by the plant can be about two to about 500 ounces of the crosslinked or uncrosslinked polymeric amino acid per acre. Crops with an abundance of foliage, such as wood crops, grain  
20 crops, cotton, etc., usually are treated at dosage rates in an intermediate range, i.e., about 25 to about 250 ounces per acre. Relatively lower dosage rates within the foregoing overall range, i.e., about two to about 25 ounces per acre, usually are sufficient for agricultural  
25 row crops, flowering nursery crops, and the like.

          The polymeric amino acid or crosslinked polymeric amino acid can be made available to the plant as a separate treatment, or in combination with water-soluble, non-peptidal polymers and/or in  
30 combination with nutrients (fertilizers). Substantially solid as well as liquid dosage forms can be utilized for this purpose, e.g., aqueous solutions, solid soil conditioning substances such as particulate clays bearing the polymeric amino acid commingled with

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nutrient components, solid particulate admixtures of polymeric amino acid, nutrient and the like.

The present invention is further illustrated by the following examples which demonstrate more efficient utilization of plant growth nutrients.

EXAMPLE 1: More Efficient Usage of  
Nutrients in Corn Plants

White corn (Early Sunglow; George W. Park Seed Co., Greenwood, SC) was grown in a greenhouse in one gallon pots filled with Fafard 3B potting soil. To each pot was added Peters™ 20-20-20 fertilizer in an amount representing a full dose of nutrients or a 1/3 dose of nutrients. A portion of the pots so treated also received an aqueous solution of polyaspartic acid (PA) (50 ml; 10 ppm by weight of PA having a weight average molecular weight (Mw) of about 3,000-5,000. The growth rates of the white corn plants in these pots were monitored, and representative plants were photographed 40 days after planting. These photographs are depicted in FIGURES 1 through 4.

These Figures show that the availability of PA to the plant enhanced plant growth at a reduced nutrient level, i.e., corn plants treated at one-third of the nutrient level but with 10 ppm of PA added (FIGURE 4) show greater growth than corn plants with the full amount of nutrient. Corn plants grown using the full nutrient level also undergo enhanced growth when 10 ppm of polyaspartic acid is used along with the nutrient (FIGURE 3). Both tests demonstrate a more efficient utilization of nutrients for plant growth.

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EXAMPLE 2: Effects of Polyaspartic Acid on  
Growth Patterns of Corn Plants  
With No Added Fertilizer

White corn (Early Sunglow; George W. Park Seed Co., Greenwood, SC) was grown in a greenhouse in one gallon pots filled with Fafard 3B potting soil. No fertilizer was added to each pot. A portion of the pots so treated received aqueous solutions of polyaspartic acid (PA) of varying dosage levels (50 ml of solution; 1 ppm, 10 ppm, 100 ppm, and 1,000 ppm of PA having a Mw of about 3,000-5,000. The growth rates of the white corn plants in these pots were monitored on a weekly basis and the data is shown in Table I, below.

**TABLE I**  
**GROWTH PATTERNS OF EARLY SUNGLOW CORN;**  
**NO ADDED FERTILIZER; SINGLE TREATMENT**

Dosages of PA	Height Change (inches)			
	Week 1	Week 2	Week 3	Week 4
Control (No PA)	13.0	9.0	6.4	5.2
1 ppm	12.5	9.4	5.4	5.7
10 ppm	11.6	11.0	5.0	7.0
100 ppm	11.4	10.4	6.4	7.2
1000 ppm	10.4	10.4	5.6	7.8

The data shown in Table I indicates that after one week of growth, corn plants with no added fertilizers but with PA added in dosages of 1 to 1,000 ppm received no benefit from PA treatment. After week 2 of corn plant growth, a beneficial effect was shown at all four dosage levels of PA. After three weeks of growth, only the 100 ppm dosage level of PA showed a benefit over no PA treatment. Finally after four weeks of corn plant growth, a low level of plant growth was

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occurring but increased growth rate was observed with all four dosage levels of PA. In summary, during the initial stage (first week) of corn plant growth PA did not increase growth rate without added fertilizer.

5 However, after the next three weeks of growth of the plant, PA treatment was beneficial to plant productivity, based on growth, even without added fertilizer. These results indicate that more efficient utilization of existing nutrients in the soil has  
10 occurred.

EXAMPLE 3: Effects of Polyaspartic Acid on  
Potassium Uptake in Early Sunglow  
Corn With No Added Fertilizer

15 White corn (Early Sunglow; George W. Park Seed Co., Greenwood, SC) was grown in a greenhouse in one gallon pots filled with Fafard 3B potting soil. No fertilizer or potassium source were added to the pots. The pots were treated with varying dosages of polyaspartic acid (PA) of about 3,000-5,000 Mw, as in Example 2.  
20 After a 40 day growing period, the plants were harvested and potassium content of the plants was determined.

TABLE II

25 **EFFECT OF POLYASPARTIC ACID ON POTASSIUM UPTAKE; EARLY SUNGLOW CORN; NO ADDED FERTILIZER; SINGLE TREATMENT/SOIL**

	Dosage of Polyaspartic Acid Used	% Potassium In Corn Plants	% Increase of Potassium In Corn Plants
30	0 ppm	2.6	—
	1 ppm	2.7	3.8
	10 ppm	3.0	15.4
	100 ppm	2.8	7.7
35	1000 ppm	3.2	23.1

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The data reported in Table II shows that a more efficient uptake of potassium by the corn plants resulted when PA was used without added fertilizer. At the 1,000 ppm dosage level, a 23.1% increase in potassium content was found in the corn plants.

EXAMPLE 4: Effect of Polyaspartic Acid on  
Phosphorous Uptake in Early Sunglow  
Corn With No Added Fertilizer

White corn (Early Sunglow; George W. Park Seed Co., Greenwood, SC) was grown in a greenhouse in one gallon pots filled with Fafard 3B potting soil as in Examples 2 and 3. No fertilizer or phosphorus containing compounds were added to the pots. The pots were treated with varying dosages of polyaspartic acid (PA) (Mw 3,000-5,000) as in Examples 2 and 3. After a 40-day growing period, the plants were harvested and phosphorus content of the plants was determined. Results from this study are shown in Table III, below.

TABLE III

EFFECT OF POLYASPARTIC ACID ON PHOSPHORUS  
UPTAKE; EARLY SUNGLOW CORN; NO ADDED  
FERTILIZER; SINGLE TREATMENT/SOIL

Dosage of Polyaspartic Acid Used	% Phosphorus In Corn Plants	% Increase of Phosphorus In Corn Plants
0 ppm	0.3	—
1 ppm	0.36	20.0
10 ppm	0.34	13.3
100 ppm	0.38	26.7
1000 ppm	0.44	46.7

The results listed in Table III show that use of PA at all dosage levels tested increased phosphorus

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uptake by corn plants when no fertilizer was added. This indicates that a more efficient utilization of phosphorus sources existing in the soil has occurred. At the highest dosage level of PA, a 46.7% increase in phosphorus uptake by the corn plants was observed.

EXAMPLE 5: Effect of Polyaspartic Acid on  
Zinc Uptake in Early Sunglow  
Corn With No Added Fertilizer

White corn (Early Sunglow) as was used in Examples 2, 3 and 4 was grown as before without added fertilizer. Again the same dosages of polyaspartic acid (PA) treatment for the corn plants was used as in Examples 2, 3 and 4. After a 40-day growing period, the plants were harvested and zinc content of the plants was determined. Results from this study are listed in Table IV, below.

TABLE IV

**EFFECT OF POLYASPARTIC ACID ON ZINC  
UPTAKE; EARLY SUNGLOW CORN; NO ADDED  
FERTILIZER; SINGLE TREATMENT/SOIL**

Dosage of Polyaspartic Acid Used	Zinc In Corn Plants, ppm	% Increase of Zinc In Corn Plants
0 ppm	29	—
1 ppm	48	65.5
10 ppm	45	55.2
100 ppm	54	86.2
1000 ppm	79	172

The above results from Table IV indicate that PA effectively increased the uptake of zinc in corn plants with no use of additional fertilizer. Even at a low dosage level of 1 ppm PA, a 65% increase in zinc



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uptake was observed. At a dosage of 1000 ppm of PA, a 172% increase in zinc uptake was found, further demonstrating the ability of PA to efficiently increase utilization of zinc in plant soil.

5

EXAMPLE 6: Effect of Polyaspartic Acid to  
Increase Plant Utilization of  
Limited Amounts of Nutrients

Duckweed (Lemna Minor L.) was grown in tap  
water containing as nutrient media a solution of  
Peters™ 20-20-20 fertilizer<sup>1</sup> (3g/1.2L) and a 1/4-  
strength solution (750 mg/1.2 L) with and without 50 ppm  
by weight polyaspartic acid (PA). The nutrient media  
were adjusted to pH value of about 6.0. The Mw of the  
PA was about 3,000-5,000 (about 22 to about 40 repeating  
units).

A single duckweed plant at the three-frond  
stage was placed in each flask. The flasks were then  
incubated under continuous light (500 lux) at  $28^{\circ} \pm 2^{\circ}\text{C}$ .  
for 21 days.

After 21 days, the plants were harvested,  
oven-dried, and weighed. Results show that nutrient  
reduction by 75% reduced plant weight by 74%, and that  
(a) no significant reduction in plant growth was found  
when PA was present in the medium with 25% nutrients  
indicating a more efficient use of a limited amount of  
nutrients and (b) plant growth was enhanced when PA was  
present in the medium with 100% nutrients. The results

---

<sup>1</sup> Total Nitrogen (N) . . . . . 20%  
3.90% Ammoniacal Nitrogen  
6.15% Nitrate Nitrogen  
9.95% Urea Nitrogen  
Available Phosphoric Acid ( $\text{P}_2\text{O}_5$ ) . . . . . 20%  
Soluble Potash ( $\text{K}_2\text{O}$ ) . . . . . 20%  
Derived from: Ammonium, Phosphate, Potassium  
Nitrate, Urea.  
Commercially available from Grace-Sierra  
Horticultural Products Company, 1001 Yosemite  
Drive, Milpitas, CA 95035.

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are presented in Table V, below. All reported values represent averages from 3 to 5 replicates.

**TABLE V**  
**RESULTS**

Treatment	Plant dry wt.-milligrams (mg)			% Change
	Expt. A	Expt. B	Average	
100% Nutrients	16.5	17.7	16.6	0
100% Nutrients + PA	21.3	22.2	21.7	31
25% Nutrients	4.7	4.0	4.4	-74
25% Nutrients + PA	15.2	16.7	16.0	0

**EXAMPLE 7: Effect of Polyaspartic Acid on Biomass**

The procedure described in Example 6, above, was followed except that a chemically defined nutrient medium having the composition described in U.S. Patent No. 4,813,997 to Kinnersley et al. (Nickell's medium with Fe present as  $\text{Fe}^{2+}$  chelated with EDTA) was used. The plants were grown in five replicate flasks, harvested after 21 days, and the combined dry weight of the harvested plants was determined. The content of potassium and phosphorus in the plants and in the spent media was determined as well. The observed results are presented in Table VI, below.

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**TABLE VI**  
**CHANGES IN BIOMASS**

		Amount of Mineral ( $\mu$ g) Control/With PA		
	Treatment	Plant Biomass (mg)	Spent Media	Plants
5	100% Nutrients/100% Nutrients + 50 ppm PA	94.4/90.9		
	Potassium (K)		11,610/11,740	1540/1530
	Phosphorus (P)		1170/1140	250/280
10	25% Nutrients/25% Nutrients + 50 ppm PA	67.3/89.3		
	Potassium (K)		2420/1170	990/1530
	Phosphorus (P)		334/322	125/173
	12.5% Nutrients/12.5% Nutrients + 50 ppm PA	54.1/62.7		
15	Potassium (K)		955/718	769/942
	Phosphorus (P)		190/192	89/111

The above results show that nutrient concentration reduced by 75% caused a 29% reduction in plant biomass (94.4-67.3) and a 36% reduction in the potassium content of plants (1540-990). However, in the same treatments containing polyaspartic acid the plant biomass was barely reduced (90.9-89.3), and the potassium content was unchanged. Analysis of the spent media showed much less potassium in the media containing PA. This data also indicates that the polymers had increased the uptake of potassium into plants.

The above results also show a remarkably good correlation between potassium content and plant-biomass as can be seen in Table VII, below.

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**TABLE VII**  
**CORRELATION BETWEEN POTASSIUM CONTENT AND BIOMASS**

	Nutrient Amount	Nutrients		Nutrients + PA	
		Biomass (mg)	K (mg)	Biomass (mg)	K (mg)
5	100%	94.4	1.54	90.9	1.53
	25%	67.3	0.99	89.3	1.53
	12.5%	54.1	0.77	62.7	0.94

10 Potassium is the most important metal needed for plant growth, and is the principal metal component of most fertilizers. However, heretofore no agent was known able to simultaneously increase the growth and potassium content of plants.

15 **EXAMPLE 8: Plant Content of Nutrients**

The content of other nutrients in plants from the full strength and 1/4-strength treatments described in Example 7, above, was determined. The observed results are set forth in Table VIII, below.

20

**TABLE VIII**  
**PLANT NUTRIENT CONTENT**

	Elements	Amount, micrograms ( $\mu$ g)		
		100% Nutrients	25% Nutrients	25% Nutrients + 50 ppm PA
25	Zn	9.2	2.6	3.7
	Mg	70	43	49
	Fe	2.5	1.0	5.9
	Ca	340	172	243
30	Cu	3.9	3.7	3.2
	Mn	4.1	1.1	1.1
	Biomass, mg	94.4	67.3	89.3

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These results show that the content of most other minerals needed for plant growth was also greatly increased by the presence of PA. Particularly noteworthy is the substantial increase in the iron content at reduced nutrient level.

EXAMPLE 9: Effect of Polyaspartic Acid to Increase Plant Utilization of Limited Amounts of Nutrients

Duckweed (Lemna minor L.) was grown in tap water under conditions described in Example 6, above, and containing as nutrient media a solution of Peters™ 20-20-20 fertilizer at full strength (100% nutrients), half strength (50% nutrients), and one-quarter strength (25% nutrients), with and without 50 ppm polyaspartic acid (PA) (Code DGI-KI) of about 3,000-5,000 Mw.

The plants were harvested, oven dried, and weighed after 21 days. The average plant dry weight is reported in Table IX, below. All reported values represent 12 to 20 replicates.

**TABLE IX**  
**RESULTS**

	<b>Treatment</b>	<b>Average Plant Dry Wt. milligrams (mg)</b>
25	100% Nutrients	15.5
	100% Nutrients + PA	20.2
	50% Nutrients	8.8
	50% Nutrients + PA	15.1
30	25% Nutrients	3.7
	25% Nutrients + PA	9.9

The foregoing results are depicted graphically in FIGURE 5. These results show that the addition of PA permits decreasing the nutrient level by about 50%

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without a significant decrease in plant growth. From  
FIGURE 5 it can also be seen that while the addition of  
PA to the nutrient solution increased plant growth at  
all nutrient levels, the effect of PA was much greater  
at the relatively lower levels of nutrients.

Specifically, an increase in plant growth of about 168%  
was noted when PA was added to a 25% nutrient solution,  
and an increase of about 29% was noted when PA was added  
to a 200% nutrient solution. Therefore, when limited  
amounts of nutrients were available for plant growth,  
use of PA increased the efficiency of usage of these  
nutrients.

EXAMPLE 10: Effect of Polyaspartic Acid to  
Increase Bean Plant Utilization  
of Limited Amounts of Nutrients

Garden beans (Mayo's Red Peanut Bush) were  
grown in the greenhouse in gallon pots filled with  
Fafard 3B potting soil. Ten pots were given 50 ml of a  
7,500 ppm solution of Peters™ 20-20-20 nutrient.  
Twenty pots were given 50 ml of a 2,500 ppm Peters™  
nutrient solution, and 10 of these pots were also given  
four weekly treatments of 50 ml aliquots of a 1 ppm  
solution of PA in water. When the bean plants flowered,  
they were taken outside for insect pollination. The  
beans that grew were harvested. The weight of beans on  
each plant was then determined. Results in Table X,  
below, show that PA increased reproductive growth  
results in a greater weight yield of beans from each  
plant. The increase in bean yield in the 1/3 fertilizer  
treatment with PA compared to the fertilizer alone, wa  
statistically significant with Duncan's multiple range  
test.

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**TABLE X**  
**YIELD OF BEANS**

	Treatment	Average Fresh Weight of Beans/Plant, g
5	100% Nutrients	6.4
	33% Nutrients	3.9
	33% nutrients + 1 ppm PA	7.2

10                   The foregoing data show that when one-third  
the regular nutrient level was used along with 1 ppm of  
PA, the average fresh weight of bean/plant increased by  
85%. This was a greater yield than was obtained when  
the 100% nutrient level was used. Under the conditions  
15 of limited nutrient availability, use of PA increased  
the efficiency of nutrient utilization resulting in  
increased bean yields.

20           EXAMPLE 11: Effect of Polyaspartic Acid to  
Increase Rapeseed Plant Utilization  
of Limited Amounts of Nutrients

A fast growing variety of rapeseed (Brasica  
rapus) was obtained from the Crucifer Genetics  
Cooperative at the University of Wisconsin. This  
25 variety was grown in 9-cm pots in a greenhouse. Pots  
were given 50 ml of a full strength solution of Peters™  
20-20-20 nutrient (7,500 ppm) in water, or the same  
volume of a 3,750 ppm solution in water. Some of the  
pots were given 50 ml of a 2 or 20 ppm solution of  
30 polyaspartic acid (PA) in water as a single treatment.  
Plants were pollinated by hand when they flowered.  
Mature seed pods were harvested. The observed results  
are reported in Table XI, below.

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**TABLE XI**  
**RAPESEED HARVEST**

	Treatment	Average # Pods per Plant	Average Dry Weight of Pods per Plant, mg
5	Full Nutrient	3.8	202
	50% Nutrient	2.9	174
	50% Nutrient + 2 ppm PA	4.8	283
10	50% Nutrient + 20 ppm PA	5.2	290
	Full Nutrient + 2 ppm PA	5.0	271

The above results show that average grain yield was higher in plants given PA than in plants receiving nutrient alone. PA increased grain yield in plants given both full and 1/2 strength nutrient. In many plants yield was higher for plants given 1/2 strength nutrient + 2 ppm PA than in plants receiving full fertilizer alone. This result shows that use of PA increased the efficiency of utilization of a limited amount of nutrients available to the rapeseed plants.

**EXAMPLE 12: Effect of Polyaspartic Acid on  
Duckweed Plants Grown in Tap Water**

Duckweed was grown in tap water and in tap water solutions of polyaspartic acid (PA) following the procedure described in Example 6, above. Table XII, below, presents the compositions of the aqueous growth medium and the observed corresponding results. In each growth medium containing nutrients, the nutrient was Peters™ 20-20-20, and in each solution containing PA, the concentration of PA was 50 ppm.



**TABLE XII**  
**EFFECT OF POLYASPARTIC ACID ON**  
**DUCKWEED PLANTS GROWN IN TAP WATER**

	Aqueous Growth Medium	Plant Dry Wt. (mg)	% Change
5	A. Nutrient (2.2g/L)	37	
	Nutrient (2.2g/L) + PA	78	111
	B. Nutrient (1.1g/L)	18	
	Nutrient (1.1g/L) + PA	57	217
	C. Nutrient (0.55g/L)	17	
10	Nutrient (0.55g/L) + PA	22	72
	D. Tap water only <sup>1</sup>	20	
	Tap water + PA	26	30

<sup>1</sup> There is some mineral content in tap water.

15

In the above table, each treatment dosage of nutrient combined with PA is compared to the same nutrient dosage without PA (the control) and % change in plant weight compared to the corresponding control is given. The above results show that PA was least effective at promoting plant growth when it was given with treatment D that has no added nutrients. If, in fact, PA was acting as a fertilizer, it should have been most effective (as measured by relative % change over control) when plants had no added nutrient for growth. Actually, the reverse was observed to be true. PA was only effective in promoting plant growth in conjunction with a real nutrient source. In treatment D, when no nutrient was added, use of PA still permitted increased plant growth by facilitating uptake of minerals from the tap water.

30

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EXAMPLE 13: Effect of Polyaspartic Acid on  
Duckweed Plants Grown in Deionized Water

Duckweed was grown in deionized water and in deionized water solution of polyaspartic acid (PA) following the procedure described in Example 6, above, except that the plants were harvested after four weeks instead of 21 days. Table XIII, below, presents the composition of the aqueous growth media that was used and the corresponding observed results. Because the biomass of each plant was so minimal, plants from eight replicate flasks of each treatment were combined to provide enough plant material to be weighed accurately.

TABLE XIII

**EFFECT OF POLYASPARTIC ACID ON  
DUCKWEED PLANTS GROWN IN DEIONIZED WATER**

Aqueous Growth Medium		Plant Dry Wt. (mg)	% Change
A.	Deionized water	8	
B.	Deionized water + PA (50 ppm)	2	-75

The above results show that PA did not increase plant growth when added to deionized water from which all minerals had been removed. This effect would not have been observed if PA was functioning as a fertilizer.

The tests performed with duckweed plants as described in Examples 12 and 13, above, demonstrate (a) that PA had minimal biological activity when supplied to plants grown in tap water and (b) that PA itself showed no nutrient or fertilizer activity with regard to these plants when the plants were grown in deionized water.

In U.S. Patent No. 4,839,461 to Boehmke it is stated that K, Mg, and Ca salts of polyaspartic acid are

suitable for use as fertilizers. No experimental evidence or examples are given to support this statement. The above tests with Duckweed plant in tap water and deionized water show that PA itself does not act as a fertilizer. It is likely that if the Ca, K and Mg salts of PA act as fertilizers, this activity is due to the nutrient value of Ca, K and Mg ions themselves rather than PA.

10      EXAMPLE 14:    Effect of Polyaspartic Acid  
                               on Corn Plants

White corn (Zea mays L.) seed (5145 Truckers Favorite; George W. Park Seed Co., Greenwood, SC) was planted in 8-cm black round pots with Fafard 3B potting soil. Each pot was given 0.3g, 0.15g, or 0.075g of Peters™ 20-20-20 nutrient. Five pots representing each treatment were kept as controls, five pots were given 50 ml of 5 ppm aqueous polyaspartic acid (PA) solution, and five pots 50 ml of a 500 ppm aqueous PA solution. After six weeks the plants were harvested, and the fresh weight and nitrogen content of the harvested plants was determined. The observed results are reported in Table XIV, below.

**TABLE XIV**  
**EFFECT OF POLYASPARTIC ACID ON CORN PLANTS**

	Treatment	Fresh wt., g	Average N Content, mg
5	100% Nutrients	45.8	67.6
	100% Nutrients + 5 ppm PA	46.5	75.7
	100% Nutrients + 500 ppm PA	50.2	73.2
	50% Nutrients	34.7	40.5
	50% Nutrients + 5 ppm PA	45.6	57.6
	50% Nutrients + 500 ppm PA	38.6	49.6
10	25% Nutrients	24.1	29.6
	25% Nutrients + 5 ppm PA	31.7	36.2
	25% Nutrients + 500 ppm PA	38.3	47.8

Above results show that PA enables plants to be grown with a 50% reduction in nutrients without showing any reduction in growth. Simultaneously with increasing the corn biomass, PA also increased the nitrogen content of the corn. Plants grown with 25% nutrients and 500 ppm PA contained more nitrogen than plants grown with 50% nutrients that were given twice the amount of nitrogen.

**EXAMPLE 15: Environmental Stability of**  
**Polyaspartic Acid**

A nutrient solution was made by adding Peters™ 20-20-20 nutrient (375 mg) to tap water (150 ml). The solution was divided into three aliquots. One 50-ml aliquot was maintained as a control. To another aliquot was added 1,000 ppm of polyaspartic acid, and 1000 ppm of lactic acid oligomer containing less than ten lactic acid residues and obtained by thermal condensation of 88% L-lactic acid by heating at 70°C.

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for 4 hours followed by heating under vacuum at 100°C.  
for 4 hours was added to the last 50-ml aliquot.

The turbidity of the samples were measured  
every day to ascertain the extent of microbial growth in  
each sample. Within a few days the solution containing  
the lactic acid oligomer had become milky, indicating  
microbial contamination. The sample containing  
polyaspartic acid remained substantially clear, even  
after 7 days. The observations are compiled in  
Table XV, below.

**TABLE XV**  
**TURBIDITY MEASUREMENTS**

	DAYS				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Control	0	0	0	0	0
Polyaspartic Acid	-0.04	+0.25	+0.26	+0.40	+0.95
Lactic Acid Oligomer	-0.11	+2.20	+3.45	+16.5	+382.0

Results indicate that polyaspartic acid has a  
relatively longer life in the environment.

EXAMPLE 16: Nutrient Composition for  
Hydroponic Growing

An illustrative aqueous composition suitable  
for incorporating polyamino acid or a crosslinked  
polyamino acid embodying the present invention and well  
suited for hydroponic farming is set forth in Table XVI,  
below.

**TABLE XVI**  
**HYDROPONIC GROWING MEDIUM**

	Nutrients	ppm by weight
5	Nitrogen as N	50
	Phosphorus as P	48
	Potassium as K	210
	Magnesium as Mg	30
	Sulfates as $\text{SO}_4^{-2}$	117
10	Sodium as Na	3.619
	Chlorides as Cl	0.04
	Iron as Fe	3
	Zinc as Zn	0.15
	Copper as Cu	0.15
15	Boron as B	0.5
	Manganese as Mn	0.5
	Molybdenum as Mo	0.1
	<u>Water, q.s.</u>	

20      **EXAMPLE 17:**      Stress Protection and Enhanced Plant  
Productivity by Crosslinked  
Polyaspartic Acid

Duckweed (Lemna minor L.) was grown in an aqueous solution containing relatively low levels of nutrients as shown in the following Table XVII.

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**TABLE XVII**  
**LOW NUTRIENT COMPOSITION**

	Nutrient Element	Concentration (ppm as element)
5	Nitrogen (N)	12.5
	Phosphorus (P)	3
	Potassium (K)	12
	Calcium (Ca)	10
10	Magnesium (Mg)	4
	Sulfur (S)	14
	Iron (Fe)	1
	<u>Water</u> , q.s.	

15

Tests were performed in which the plants were grown in separate flasks under controlled conditions employing the low nutrient solution which was enhanced by the addition of 50 ppm by weight of a selected crosslinked polyaspartate, identified as Compound A or B in Table XVIII, below. Compound A represents a polyaspartate in which the crosslinked polyamino acid is crosslinked with an organic divalent base and Compound B represents a polyaspartate in which the crosslinked polyamino acid is crosslinked by free radical technique with hypophosphite.

20

25

TABLE XVIII  
POLYASPARTATE COMPOUND

- 5           A. sodium salt of polyaspartic acid,  
            crosslinked with 10 mol% meta-xylylenediamine  
            (Mw about 80,000)
- 10          B. 80 mol% aspartic acid/20mol%  
            N-allylaspartamide copolymer, free radical  
            crosslinked with hypophosphite, sodium salt  
            (Mw about 53,311)

15           For evaluating stress protection, a similar  
            series of tests were performed in which the plants were  
            grown employing each of the foregoing compositions to  
            which 3 ppm of Cu<sup>++</sup> ion was also added. For each test,  
            the enhanced nutrient solution was adjusted to pH 6.7 ±  
            0.1 and five replications were performed for each  
            compound tested, both with and without the added copper.

20           A single duckweed plant at the three-frond  
            stage was placed in each of five flasks. The flasks  
            were then incubated under continuous light (natural  
            light supplemented by metal halide lights; photon flux  
            density 500 micromoles per m<sup>2</sup> per sec.) in a greenhouse  
25           at a temperature of about 28° ± 2°C. for three days.  
            The plants were then harvested after three days, oven  
            dried to constant weight at 80°C and weighed. The  
            average plant dry weight per replicate is reported in  
            Table XIX, below. All reported values represent the  
30           averaged weight of the five replicates.



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**TABLE XVIX**  
**STRESS PROTECTION AND PLANT PRODUCTIVITY**

<u>AVERAGE BIOMASS (mg)</u>				
Compound	No Cu <sup>++</sup>	% Imp.*	3 ppm Cu <sup>++</sup>	% Imp.*
None (Control)	9.648		3.338	
A	11.03	14	4.646	39
B	11.6	20	4.872	46

\* % Improvement shows increase in average biomass weight when crosslinked polyaspartate is present over that of the control.

The data show that the addition of either one of the crosslinked polyaspartates to the low level nutrient solution resulted in enhanced plant productivity based on an average biomass increase of more than 10%. The data also show that the stressing effect of copper toxicity decreased the biomass of the control by 65%. In contrast the presence of either one of the crosslinked polyaspartates afforded a degree of stress protection by reducing the limiting effect of the copper toxicity to about 57-58%. Thus, the crosslinked polyaspartate enhanced plant productivity by more than one-third.

The foregoing specification and the Examples are intended to illustrate the present invention, but are not to be taken as limiting.

WE CLAIM:

1. A method for enhancing plant productivity by supplying to the plant a composition containing a productivity enhancing amount of a crosslinked polyamino acid characterized by being water soluble and having a weight average molecular weight larger than about 1,500.
2. The method of claim 1 wherein the composition supplied is in the form of an aqueous liquid.
3. The method of claim 1 wherein the composition supplied is in a substantially solid form.
4. The method of claim 1 wherein the crosslinked polyamino acid is supplied separately or in combination with a fertilizer.
5. The method of claim 1 wherein the composition supplied contains a water-soluble, non-peptidal polymer.
6. The method of claim 1 wherein the crosslinked polyamino acid is derived from a crosslinkable polyamino acid or salt thereof selected from the group consisting of polyaspartic acid, polyglutamic acid, polylysine, polyglycine, polycysteine, polyserine, block copolymers thereof, random copolymers thereof, terpolymers thereof, and mixtures thereof.
7. The method of claim 1 wherein the crosslinked polyamino acid is crosslinked polyaspartic acid or salt thereof.
8. The method of claim 7, wherein the crosslinked polyaspartic acid has a weight average molecular weight of at least about 2,000.
9. The method of claim 1, wherein the crosslinked polyamino acid is derived from polyaspartic acid having aspartic acid residues of at least 20% of the total number of residues in the polymer.

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10. The method of claim 1 wherein the composition supplies crosslinked polyamino acid in an amount of 10 parts per billion by weight.

5 11. The method of claim 1 wherein the crosslinked polyamino acid is derived from a crosslinked polysuccinimide.

12. The method of claim 1 wherein a crosslinked precursor of a polyamino acid is supplied to the plant and hydrolyzed in situ.

10 13. The method of claim 1 wherein the crosslinked polyamino acid is crosslinked with an organic base.

14. The method of claim 13 wherein the crosslinked polyamino acid is polyaspartic acid crosslinked with meta-xylylenediamine.

15 15. The method of claim 14 wherein the crosslinked polyamino acid is a salt of polyaspartic acid crosslinked with 10 mol% meta-xylylenediamine and has a weight average molecular weight of about 80,000.

20 16. The method of claim 1 wherein the crosslinked polyamino acid is free radical crosslinked.

17. The method of claim 16 wherein the crosslinked polyamino acid is free radical crosslinked with hypophosphite.

25 18. The method of claim 17 wherein the crosslinked polyamino acid is a salt of a copolymer of 80 mol% aspartic acid/20 mol% N-allylaspartamide copolymer and has a weight average molecular weight of about 53,311.

30 19. A method for enhancing plant productivity by supplying to the plant a composition containing a productivity enhancing amount of a crosslinked polysuccinimide.

35 20. An improved composition for enhancing plant productivity containing a fertilizer together with

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a productivity enhancing amount of a crosslinked polyamino acid which is water soluble and has a weight average molecular weight larger than about 1,500.

21. The composition of claim 20 wherein the crosslinked polyamino acid is derived from a polyamino acid selected from the group consisting of polyaspartic acid, polyglutamic acid, polylysine, polyglycine, polycysteine, polyserine, block copolymers thereof, random copolymers thereof, terpolymers thereof and mixtures thereof.

22. The composition of claim 20 wherein the crosslinked polyamino acid is present in an amount of at least about 10 parts per billion by weight of the composition.

23. The composition of claim 20 wherein the crosslinked polyamino acid is crosslinked polyaspartic acid or salt thereof.

24. The composition of claim 20 wherein the crosslinked polyamino acid is derived from hydrolyzable crosslinked polysuccinimide.

25. The composition of claim 20 wherein the crosslinked polyamino acid is crosslinked with an organic base.

26. The composition of claim 20 wherein the crosslinked polyamino acid is polyaspartic acid crosslinked with meta-xylylenediamine.

27. The composition of claim 20 wherein the crosslinked polyamino acid is a salt of polyaspartic acid crosslinked with 10 mol% meta-xylylenediamine and has a weight average molecular weight of about 80,000.

28. The composition of claim 20 wherein the crosslinked polyamino acid is free radical crosslinked.

29. The composition of claim 20 wherein the crosslinked polyamino acid is free radical crosslinked with hypophosphite.

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30. The composition of claim 20 wherein the crosslinked polyamino acid is a salt of a copolymer of 80 mol% aspartic acid/20 mol% N-allylaspartamide copolymer and has a weight average molecular weight of about 53,311.

31. The composition of claim 20 including a water-soluble, non-peptidal polymer.

32. The composition of claim 20 in the form of an aqueous liquid.

33. The composition of claim 20 in the form of a solid.

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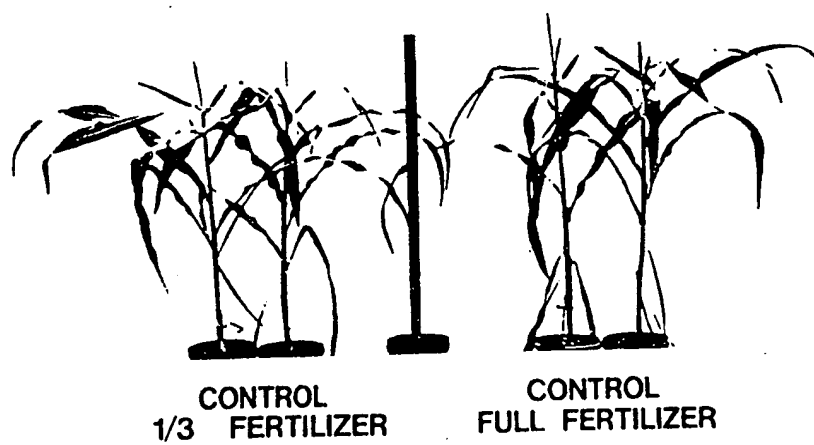


FIG. 1

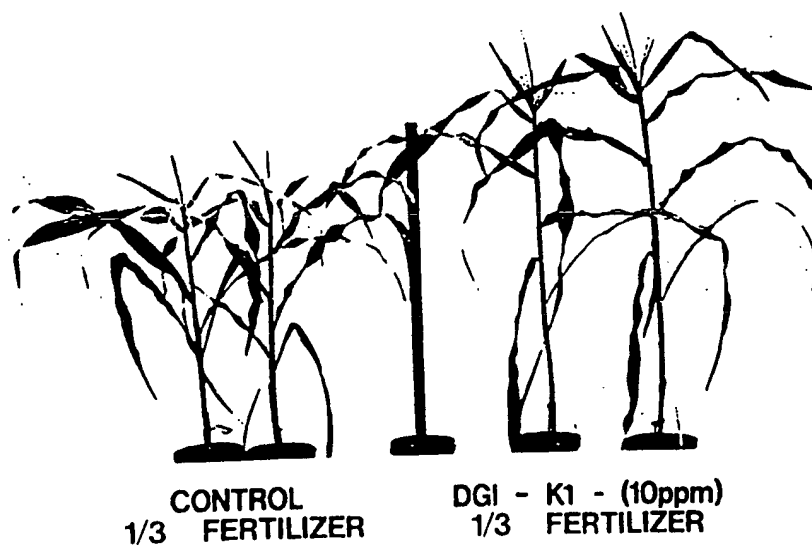


FIG. 2

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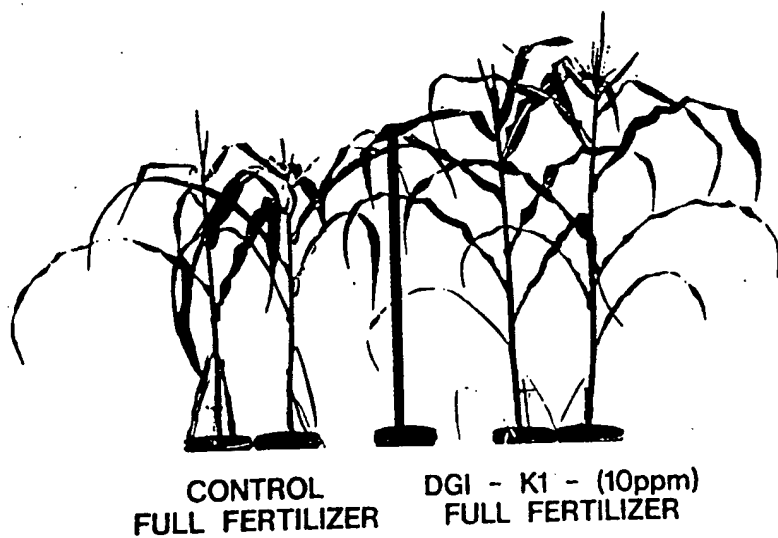


FIG. 3

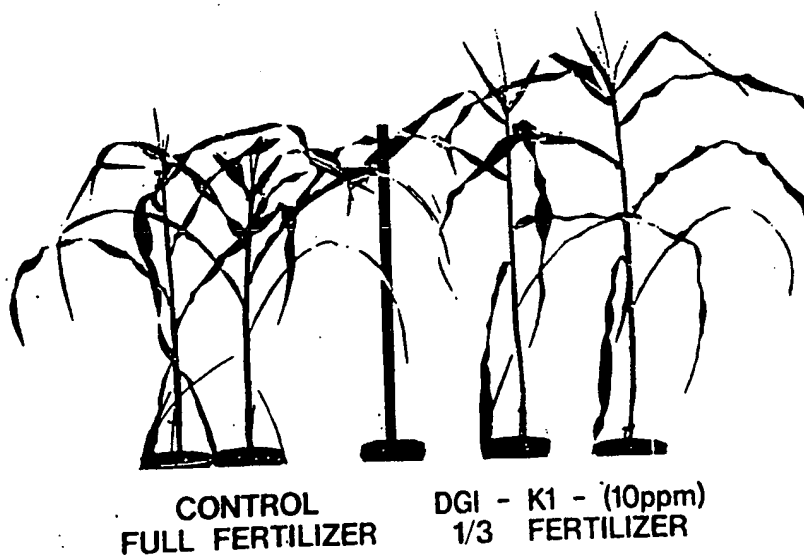
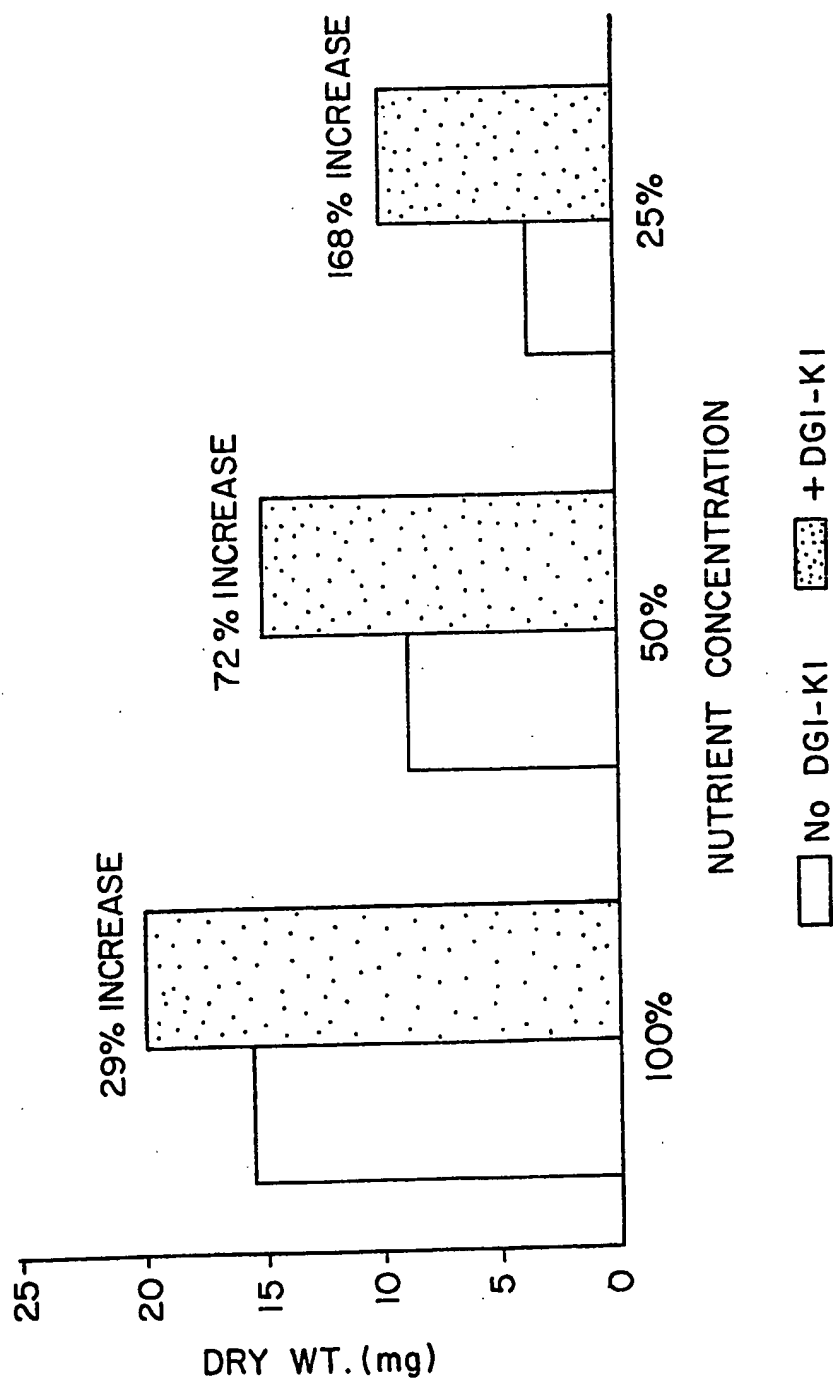


FIG. 4

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FIG. 5





# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/00501

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A01N 37/18; C05G 3/00

US CL : 504/149, 283, 320, 335

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 504/149, 283, 320, 335

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS: polyamino, asp, glu, lys, gly, cys, ser (etc.)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,839,461 A (BOEHMKE) 13 June 1989, see entire document.	1-33
Y	US 4,590,260 A (HARADA ET AL.) 20 May 1986, see entire document.	1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*A*	document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E*	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O*	document referring to an oral disclosure, use, exhibition or other means	*Z*	document member of the same patent family
*P*	document published prior to the international filing date but later than the priority date claimed		

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